DOES CONCRETE SELF-DECONTAMINATE VX?

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ABSTRACT

A preliminary study has been done to examine the sorption and reaction of VX in an aged sample of concrete using ^{31}P NMR. Facile sorption of neat liquid VX into concrete is observed. The half-life for this process is about 2 min, and is attributed to VX penetrating the surface pores to form a sorbed phase tentatively assigned to a solid protonated form of VX. Once sorbed, the VX slowly hydrolyzes to non-toxic ethyl methylphosphonic acid (EMPA) with a half-life of about 3 months. Closer examination of the reaction of neat liquid VX with crushed concrete reveals a two-step behavior in the kinetics. An initial reaction with a half-life of about 2 h consumes 12% of the VX. After about 1 h, a much slower steady state hydrolysis ensues exhibiting a half-life of 28 days. EMPA is the sole hydrolysis product detected in the ^{31}P MAS NMR spectra; no toxic EA-2192 is observed. Considering the concrete surface area, one monolayer would accommodate 13% of the applied VX. Thus the observed kinetic behavior is consistent with the concrete surface possessing a limited reactive capacity corresponding to about one VX monolayer.

INTRODUCTION

The nerve gas VX, O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate, exhibits peculiar behavior when applied to concrete. Contrary to other agents such as GD, pinacolyl methylphosphonofluoridate (Soman), and HD, bis (2-chloroethyl) sulfide (mustard), detectable levels of VX vapor diminish quite rapidly for this agent deposited on concrete.[1] Two possible explanations for this observation are that either VX is rapidly decontaminated by concrete, or that VX sorbs intact but in a manner such that off-gassing does not occur. Of course it is important to determine which is indeed the case. In the current study, ^{31}P NMR is used to examine the behavior of VX in an aged sample of concrete. NMR is employed as an in situ technique, which allows species to be detected on both the surfaces of materials, and throughout their bulk. Further, this method avoids the problem of tenuous extraction procedures.

In a recently published paper, Groenewold et al.[2] examined the fate of dilute VX solutions (1 μg/mL) applied in sub-monolayer loadings on crushed concrete samples by ion trap secondary ion mass spectrometry (IT-SIMS). Single, small droplets of neat VX (0.01 μL) applied to small concrete chips were also examined. Within an hour after application, extremely low levels of VX could be detected (5 ng on a concrete chip). However, on aged samples, expected reaction products were observed consistent with rapid VX degradation. Indeed, intact VX was not observed after a day or so. Whereas these results demonstrate facile reactions for evenly-spread, sub-monolayers of VX and 0.01 μL droplets on concrete, much larger droplets, perhaps as large as 2.0 μL, are considered probable in the event of a CWA attack.[3] Moreover, terrorist activities or accidental spills at storage facilities could involve even larger droplet sizes and depositions. Using the identical concrete employed by Groenewold et al.,[2] the current study examines VX droplets on the order of several μL to determine the behavior of VX on concrete in this vicinity of the droplet size spectrum.

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RESULTS AND DISCUSSION

VX ON CONCRETE CHUNK

The ^{31}P NMR spectrum[4] obtained 11.8 min after the addition of 15 μL VX to a 737 mg chunk of concrete is shown in Figure 1. Two features are evident in the spectrum: a small sharp peak at 47.7 ppm centered on a much broader peak. During the 9 min scan time required to obtain the spectrum, the intensity of the sharp peak was observed to decrease. This behavior leads to the assignment of the sharp peak to unprotonated VX residing in a rather liquid-like surface film and the broad peak to protonated VX in a less-mobile sorbed phase within the concrete pores, respectively (further comments on VX protonation and the nature of the sorbed phase are given below). Thus the quite rapid sorption of VX into the concrete pores is readily observed by NMR. One can judge from the minuteness of the sharp peak relative to the broad peak that several half-lives must have passed during the 11.8 min elapsed time; thus the apparent half-life for the sorption on VX into the concrete chunk is on the order of 2 min. Such rapid sorption of VX into concrete is consistent with the previous observation of a rapid decrease in VX vapor concentration over concrete to which VX droplets were applied.[1] Indeed, a half-life of 1.7 min was observed for this process.[1]

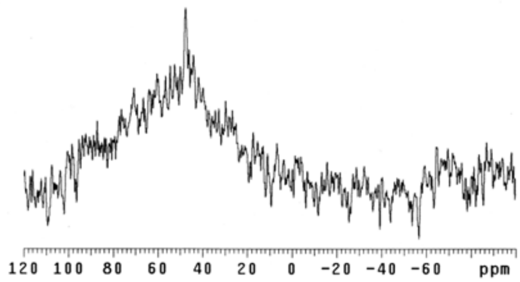
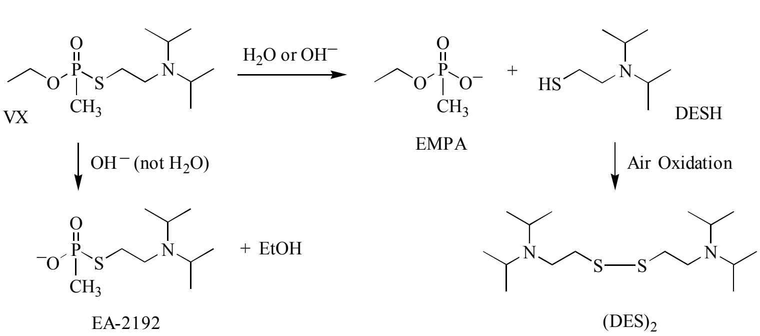


Figure 1. ^{31}P NMR spectrum obtained 11.8 min after the first addition of 15 μL of neat VX to the 737 mg concrete chunk.

After a few weeks, liquid condensate was observed on the inside of the 10 mm NMR tube in the vicinity of the concrete chunk. The condensate was dissolved in acetonitrile and analyzed by ^{31}P and ^{13}C NMR which revealed the expected VX hydrolysis products (Scheme 1) ethyl methyl phosphonic acid (EMPA), diisopropylaminoethanethiol (DESH), and/or bis(diisopropylaminoethane)disulfide [(DES)2], but not VX itself. These same products were also detected by Groenewold et al.[2] using IT-SIMS. Importantly, no toxic EA-2192 was observed in the condensate. As shown in Scheme 1, EA-2192 forms during basic hydrolysis but not in the reaction of VX with a stoichiometric amount of water.[6] The EMPA, DESH and (DES)2 products are apparently not strongly held in the concrete and are freely expelled. However, the relative non-volatility exhibited by concrete-sorbed VX is consistent with it residing in a solid-like phase (to be discussed further below).

Scheme 1



After several months, a second 15 μL addition of VX to the concrete was done to capture the disappearing behavior of the sharp peak. These spectra are shown in Figure 2. This time the VX sorption

was somewhat slower; perhaps owing to product clogging the pores. Also, two sharp peaks were evident in the spectra: one at ca. 60 ppm and the other at ca. 46 ppm. As before, the 46 ppm peak is due to the liquid surface film which disappears as VX is sorbed into the concrete pores. The more persistent peak at 60 ppm is due to a "smudge" of VX liquid on the inside of the 10 mm NMR tube which was inadvertently transferred from the concrete chunk. ^{31}P NMR shifts for VX are quite solvent dependent, with shifts ranging from 52.4[6] to 63.1 ppm.[7] Similarly, we have also observed numerous shifts for VX sorbed in various matrices, ranging from 63.6 ppm for intrazeolitic (NaY) VX[8] to 51.1 ppm for VX on nanosize CaO.[9] It is perhaps important to note that VX shifts to high frequency, i.e. > 60 ppm, are associated with environments conducive to protonation of its amine, i.e. in water[7] or in NaY zeolite,[8] whereas lower frequency shifts tend to occur in non-protonating media such as organic (aprotic) solvents, or on basic metal oxides such as CaO.[9] The shift of neat, unprotonated VX was measured to be 52.0 ppm. However, the 60 ppm shift exhibited by the VX "smudge" on the glass NMR tube is nearly identical to the 58 ppm shift found for neat VX containing sufficient water to assure protonation. Thus the VX smudge encountered sufficient adventitious water to protonate it. The 46 to 47.7 ppm shift exhibited by VX in the surface film on concrete, although distant from that of neat VX, is shifted in the correct direction anticipated for a non-protonated species. Thus in the liquid-like surface film on concrete, VX likely remains non-protonated and volatile. This is consistent with the brief, but short-lived VX vapor detected over contaminated concrete.[1]

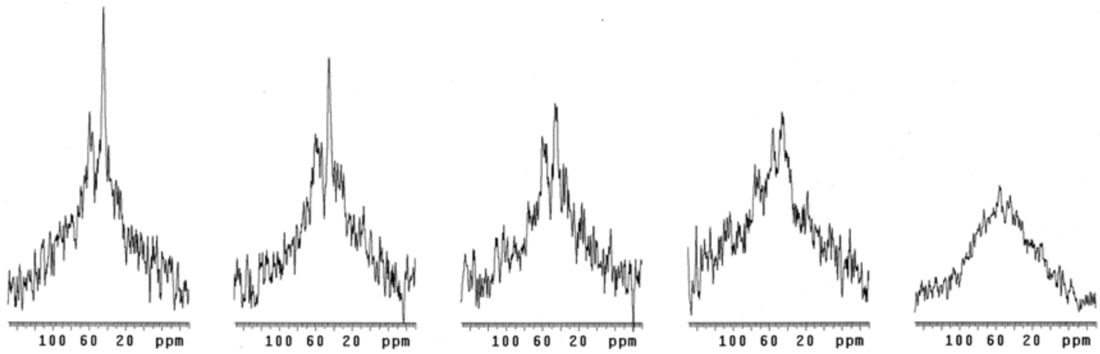


Figure 2. Selected ^{31}P NMR spectra obtained after the second addition of 15 µL of neat VX to the 737 mg concrete chunk at (left to right) 6, 8, 12, 16, and 25 min.

As shown in Figure 3, ^{31}P NMR spectra obtained over time for the initial 15 µL application show a decrease in the intensity of the broad peak for sorbed VX. As confirmed below using ^{31}P MAS NMR, the sorbed VX selectively hydrolyzes to yield EMPA. Although the EMPA peak overlaps that of VX, it is extremely broad. Thus the "sharper" peak for sorbed VX is easily distinguished. A plot of intensity of the "sharper" sorbed-VX peak vs. time is shown in Figure 4, from which a VX half-life of 96.5 days (ca. 3 months) is obtained.

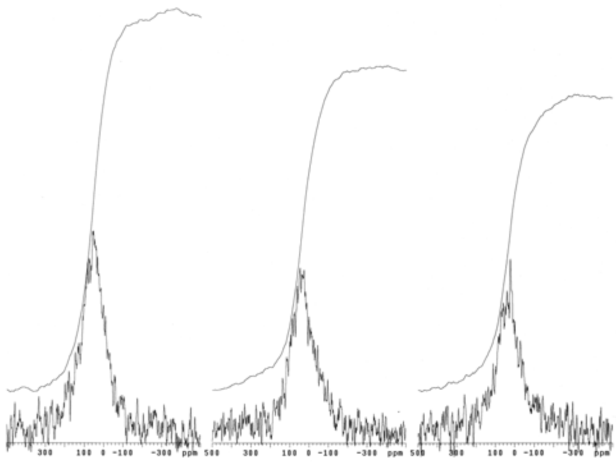


Figure 3. Selected ^{13}P NMR spectra obtained over time for the first addition of 15 µL neat VX to the 737 mg concrete chunk (left to right): 14 days, 32 days and 67 days.

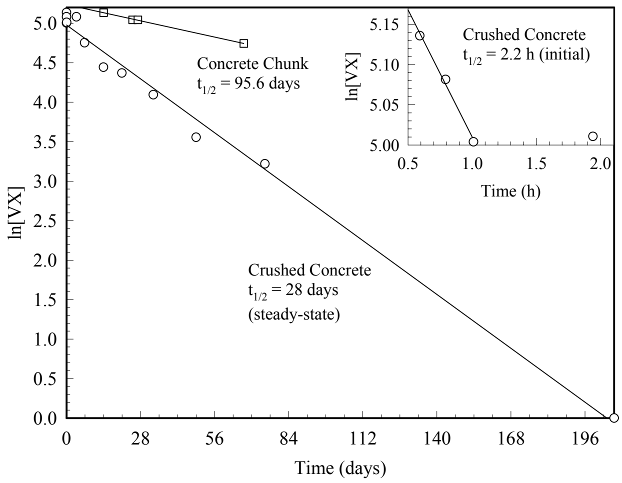


Figure 4. Reaction profiles obtained for sorbed VX in concrete. Inset shows the initial "fast" reaction for VX on crushed concrete

VX ON CRUSHED CONCRETE

^{31}P MAS NMR spectra obtained for 5 µL VX added to 293 mg crushed concrete are shown in Figure 5. On the left side of Figure 5 is an initial non-spinning (static) spectrum obtained at t = 10.5 min to verify sorption of VX prior to commencing MAS (note the lack of a sharp peak for VX in the surface film). The MAS spectrum obtained at t = 35.5 min shows a sharp peak for sorbed VX at 52.6 ppm surrounded by a manifold of spinning sidebands spaced at the spinning rate of ca. 3000 Hz. Note that the total integrated area of both spectra is identical (as expected), demonstrating that all of the VX is observable using either of the two methods.

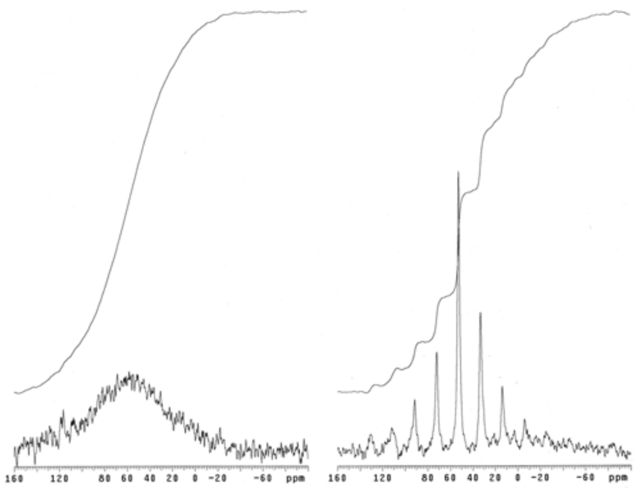


Figure 5. ^{31}P NMR spectra obtained after the addition of 5 µL neat VX to 293 mg crushed concrete: static spectrum at t = 10.5 min (left), and (right) MAS spectrum at t = 35.5 min (right).

Selected ^{31}P MAS NMR spectra obtained for the crushed sample over time are shown in Figure 6. Note the slow, but steady decrease in the intensity of the VX peak and the concomitant emergence of a broader product peak at 24.7 ppm. The shift of the broad peak is consistent with the EMPA hydrolysis product, which has previously been observed on numerous inorganic oxides.[8-10] Conspicuously absent is any detectable peak for the alternative, toxic EA-2192 hydrolysis product which would yield a peak near 42.5 ppm.[7] Rapid, basic hydrolysis of VX in solution yields about 78% EMPA and 22% EA-2192 (Scheme 1).[6,11] However, the slow reaction of VX with a limited or equimolar amount of water yields the selective formation of EMPA.[6] The

selective hydrolysis of sorbed VX to EMPA on concrete is in agreement with previous studies of other inorganic oxides,[8-10] and suggests that the "water" mechanism, or one quite similar, is operative.

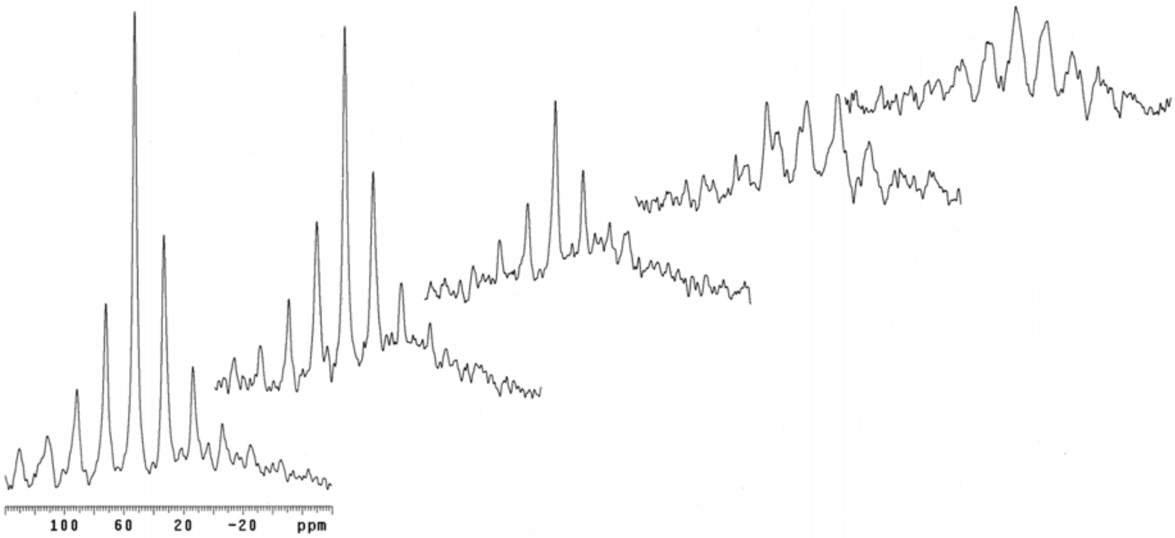


Figure 6. Selected ^{13}P MAS NMR spectra obtained over time for the addition of 5 μL neat VX to 293 mg crushed concrete (left to right): 35.5 min, 1 week, 1 month, 2.5 months and 6 months.

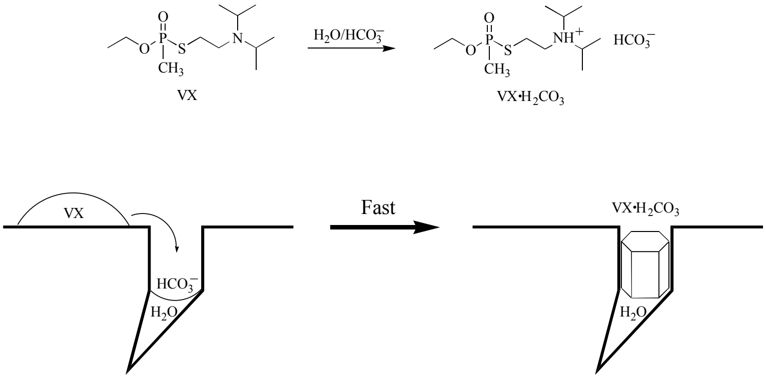
Close examination of the reaction profile shown in Figure 4 for VX on the crushed concrete reveals a two step process for the hydrolysis. Initially, a rather fast reaction exhibiting a half-life of 2.2 h consumes about 12% of the applied VX. The reaction then abruptly slows, with an ensuing half-life of 28 days. From the reported surface area of the concrete (4 m^2/g),[2] the area required by a single VX molecule (79 $Å^2$),[2] and the amount of crushed concrete (293 mg), it is calculated that one monolayer would accommodate 13% of the applied 5 μL VX. Thus the amount of VX consumed in the initial fast reaction (12%) is consistent with the monolayer capacity of the concrete surface, and implies a limited reactive capacity for about 1 monolayer of VX. This apparent reactive capacity and the ca. 2.2h half-life observed for the initial fast reaction are in agreement with the results of Groenewold et al.[2] where sub-monolayer amounts of VX were found to react within 1 day. However, once the reactive capacity is exceeded, which is evidently the case for μL-size droplets, VX remains very persistent on concrete. The observed VX half-lives for the two samples, 28 days for crushed concrete and 3 months for the concrete chunk, are quite long compared to the rate of the previously mentioned VX/water reaction, where hydrolysis was typically completed within 30 to 60 days.[6] Thus the hydration state of the concrete may be important to the overall decomposition rate, and this will be examined in future work. Also of concern is the fact that a much longer half-life was observed for the 15 μL drop on the concrete chunk compared to the 5 μL drop on crushed concrete, which implies that droplet size may be important to VX persistence. A more detailed study of droplet size effect is also planned.

SPECULATION ON THE NATURE OF CONCRETE-SORBED VX

For VX in the sorbed phase, its ^{31}P MAS NMR peak is shifted to high frequency compared to VX in the surface film, consistent with its protonation. Moreover, the intense spinning sidebands are indicative of a rather large chemical shift anisotropy (CSA)[12] expected for solid phosphonates which are not motionally-averaged.[13] Such a "solid" form of VX has not previously been observed in a variety of solid media,[8-10] and concrete appears quite unique in this regard. Thus the high frequency shift of VX in the sorbed phase and the apparent large CSA are consistent with VX in a rather rigid, protonated sorbed phase. Further work is necessary to confirm this, and ^{15}N MAS NMR studies of ^{15}N-labelled VX in concrete are planned to clearly determine the protonation state of the amine group. Also, more work is needed to generate authentic samples of protonated VX to assess the appropriateness of counter ions for generating solid VX. For example, OH^- (as in solid ammonium hydroxide, NH4OH), may not be reasonable since small amounts of water added to VX cause phase separation but no precipitate[6] (VX•H2O, although not very soluble in VX, remains in a liquid phase). A more likely suspect may be $HCO3^-$ (as in solid ammonium bicarbonate, NH4HCO3) which is

presumably ubiquitous on concrete surfaces owing to neutralization of residual caustic by ambient CO2. The protonated, hydrochloride salt of VX, i.e. VX•HCl, is known to be quite stable in storage. Facile formation of a similar solid, protonated VX species in concrete, i.e. VX•H2CO3, may indeed be contributing to the observed VX persistence and would further account for the precipitous drop in VX vapor pressure on freshly-contaminated concrete.[1] This process is represented schematically in Scheme 2, where the VX surface film quickly sorbs into pores of the concrete where it encounters adventitious water and HCO3⁻ to yield solid VX•H2CO3 (depicted as a hexagonal crystal). Finally, it should be noted that although solid, protonated VX may form in concrete, it is quite water soluble (even more so than "free-based" VX[7]) and thus would still dissolve and react in the presence of water.

Scheme 2



CONCLUSION

Concrete rapidly sorbs large droplets of VX in excess of several μL with a half-live of about 2 min. Compared to VX in the liquid-like surface film, where an extreme ^{31}P NMR shift to low frequency occurs, the shift to higher frequency for VX in the sorbed phase and the large apparent CSA suggests formation of a solid, protonated species postulated as VX•H_2CO_3. Following formation of the sorbed phase a two-step reaction is observed: a rather fast initial reaction followed by a much slower steady-state reaction. The amount of VX consumed in the initial fast reaction implies that the concrete surface possesses a limited reactive capacity corresponding to about 1 monolayer of VX. The half-life of this surface reaction is about 2.2 h. However, applied VX in excess of a monolayer is very persistent, exhibiting a half-life of 28 days to 3 months, perhaps depending on droplet size and/or surface hydration. VX hydrolysis is selective to EMPA; no toxic EA-2192 is observed. The hydrolysis products, EMPA, DESH and $(DES)_2$, freely evaporate from the surface, whereas residual VX does not (at least not to a comparable extent).

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